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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Treating Oils, Waxes and the like to Remove or Recover Substances Therefrom.

We, THE SILICA GEL CORPORATION, a corporation existing under the laws of the State of Maryland, and having a place of business at 1100, Garrett Building, 239, Redwood Street, Baltimore, Maryland, United States of America, Assignees of WALTER ALBERT PATRICK, Professor of Chemistry, The Terraces, Mount Washington, Baltimore, Maryland, United States of America, and ERNEST BALDWIN MILLER, Chemist, 1100, Garrett Building, 239, Redwood Street, Baltimore, Maryland, United States of America, both citizens of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is for improvements in and relating to the refining of oils, waxes and the like, and concerns a specific development of the invention of our prior British Letters Patent, No. 176,997.

The invention of the said prior patent is based upon the discovery that porous bodies having very fine or ultramicroscopic pores will adsorb certain solutes from solution under appropriate conditions. The pores of the type of adsorbing material utilised according to the said invention are so small that it is a difficult matter accurately to determine and define their size. For practical purposes, however, the requisite pore dimensions may be defined by reference to the amount of water that one gram of the adsorbing material will adsorb when in equilibrium with water vapour under definite conditions of partial pressure of water vapour and of temperature.

A liquid that wets a capillary tube will rise in the tube above the level of the surface of the liquid surrounding the same, the extent of the rise varying with the diameter of the tube. The vapour pressure of the liquid inside the tube is smaller than the vapour pressure at the level surface of the liquid outside the tube. This lowering of the vapour pressure by the liquid within the capillary tube is not appreciable until the diameter of the tube is extremely small, and the smaller the bore of the tube, the greater the decrease in vapour pressure.

The amount of water adsorbed by a porous body at a given temperature and partial pressure depends both upon the size of the pores and upon the total interior volume thereof. By determining the amount of a given substance, water for example, which is adsorbed by each of two porous bodies under like conditions of temperature and partial pressure, a means is provided for comparison between the size and volume of the pores in the two adsorbents. For example, one gram of silica gel has a total internal volume of about 0.41 c.c. In other words, if the pores in this gel are completely filled with water, the amount taken up will be approximately 41 *per cent.* of the initial weight of the gel. A sufficient percentage of the total internal volume in silica gel is made up of pores of such size that the gel adsorbs water to the extent that it contains about 21 *per cent.* of its own weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially 22 m.m. of mercury. On the other hand, kieselguhr, ordinary dried precipitated silica, and bone black under like conditions adsorb practically no water. It follows, therefore, that these latter substances have practically no pores as small as the greater number of the pores in silica gel.

[*Price*

It was found that materials which adsorb water to such a degree that they contain less than about 10 *per cent.* of their initial weight of water at 30° C. and under a partial pressure of substantially 22 m.m. of mercury have pores too large to make the material of any practical value for adsorbing solutes from solution. The invention of the aforesaid British Patent, No. 175,987 is therefore restricted to the use of adsorbing materials having a sufficient number of small pores to render said materials capable of adsorbing water to such a degree that they may contain not less than 10 *per cent.* of their initial weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially 22 m.m. of mercury. It has now been found that an adsorbing material having ultramicroscopic pores of the size defined is extremely effective in removing by adsorption the impurities in solution in oils, waxes and the like, provided that the adsorbing material selected has a lower surface tension towards the substance to be adsorbed than towards the oil.

According to the present invention, therefore, a process for the purification of oils, waxes and the like, by contact treatment of the crude substance with a porous body, is characterised by the selection of a porous body which has pores of such size that the said body can adsorb water to such a degree that it will contain not less than substantially 10 *per cent.* of its own weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially 22 m.m. of mercury.

As in the case of the invention of British Letters Patent, No. 175,987, the preferred adsorbing material is silica gel having a structure similar to that produced when the gel is prepared according to the method described in British Letters Patent, No. 136,543. The invention is not, however, limited to the use of silica gel, and where this gel is not utilisable, other gels or adsorbing materials may be used, for example, fully activated charcoal, gels of iron oxide, tin oxide, aluminium oxide, tungstic oxide, zirconium oxide and titanium oxide, provided that such alternative adsorbents have a sufficient number of small pores of the type defined.

By fully activated charcoal is meant a charcoal or carbon from which all the hydrocarbons have been removed so that it will adsorb water in preference to other liquids. We are aware of British Specification No. 176,476 relating to the manufacture of active carbon.

We are aware that it has been proposed to use warm oxides of iron and aluminium, also bauxite and floridin for the desulphurisation of petroleums (see British Specification, No. 186,955) but it will be understood that, as in the case of other porous adsorbers, the present invention is concerned only with metallic oxide gels which have the pore size hereinbefore defined. Such metallic oxide gels may be obtained by processes similar to that employed for the manufacture of silica gel (see for example, British Letters Patent No. 212,065).

The hard porous silica gel which is the preferred adsorbing material according to the present invention is to be distinguished from the dried gelatinous precipitate obtained, for example, by mixing an acid and sodium silicate in solution and then drying the precipitated silicic acid. The latter product does not possess the porous structure of the gel made according to Patent, No. 136,543, or by dialysis, and has not been found suitable for the adsorption of solutes from solutions. According to the said patent, solutions of an acid and a silicate are employed of such concentrations and in such quantities that the acid and the silicate will react to give a homogeneous, colloidal solution of silicic acid. Premature coagulation of the mixture is prevented by thoroughly stirring at the time of mixing the solutions. Three or four hours after mixing, a setting, without precipitation, to a homogeneous gel-like mass takes place, and after this mass is washed and slowly dried as directed in the specification a hard porous gel is obtained the pores of which are ultramicroscopic.

As pointed out in the Specification of the Patent, No. 175,987, that solute is adsorbed from a solution which exhibits the smallest surface tension towards the pore walls of the adsorbing material; in other words, the solute that more easily wets the porous material will be adsorbed. Furthermore, the separation of a new phase from the solution is easier the smaller the solubility of the substance in the solution. As a measure of solubility, the critical solution temperature may be selected, and the greatest adsorptive effect will be obtained from a solution having the highest critical solution temperature. The extent of the adsorption is also influenced by the difference in density between the components of the solution. The smaller the difference in density, the greater will be the adsorption of one of the components from the solution. These principles find application in the practice of the present invention as in that of the Patent, No. 175,987.

The present invention is applicable to

the purification of oils and waxes in general, vegetable, animal, and mineral, including benzine, toluene, carbon tetrachloride and aniline, but for convenience will be described in its application to the refining of gasoline and kerosene.

Straight run and cracked gasoline and kerosene distillates in general contain sulphur compounds, have a disagreeable or "sour" odour and a yellow colour. These features vary widely with different products, depending upon the source of the crude oil, upon whether it is a straight run distillate or a product of cracking.

The exact form in which sulphur exists in gasoline or kerosene is still open to doubt. It is well known that there are at least two forms, one of which reacts to the doctor test and one which does not. It is further known that certain gasolines and kerosenes containing sulphur and giving a negative doctor test will, after standing, give a positive test. Such a change is accelerated by heat and light, and by contact with air (oxygen) and moisture, and as a result it is often found that a gasoline or kerosene, refined by chemical treatment so as to give a negative doctor reaction, will subsequently give a positive reaction to the test.

A similar phenomenon is observed with both colour and odour. For example, a gasoline may be refined by chemical treatment, such as treatment with sulphuric acid, alkali and lead oxide, so as to give a water-white or nearly water-white product and a "sweet" odour, but on standing this apparently satisfactory product, particularly if exposed to light, moisture and oxygen, will develop a "sour" odour and a yellow colour.

The reappearance of a positive doctor test under the conditions stated appears to be connected with certain unsaturated constituents of the gasoline as well as sulphur, and these and similar changes also give rise to the "sour" odour, and result in the formation of colouring substances which remain dissolved in the gasoline imparting a yellow colour thereto.

Petroleum products, such as gasoline and kerosene, when refined in accordance with the present invention, although high in unsaturated constituents, remain colourless or water-white for an indefinite period even when exposed to light and air. These refined hydrocarbons having more than 10 *per cent.* of unsaturated hydrocarbons and a sulphur content below 0.02 *per cent.*, which remain colourless indefinitely, are new products. The proportion of unsaturated hydrocarbons may be determined by reaction with 93 *per cent.* sulphuric acid. No known refined petroleum product having over 10 *per cent.* of unsaturated hydrocarbons and giving a negative gum test has hitherto been made. The gum test consists in evaporating to dryness 100 c.c. of the sample in a polished copper dish. For a negative test there should be no discolouration of the dish and no deposit. The product obtained by refining sufficiently according to the present invention gives a negative gum test, and in this respect, in addition to the others mentioned, the product is new.

In carrying the invention into effect, the crude petroleum product is refined by bringing it into intimate contact with the adsorbing material, preferably in powdered condition, and allowing and maintaining contact between the liquid and the adsorbing material until the objectionable components of the liquid are adsorbed to the degree desired, and thereafter separating the material and the refined product.

The crude liquid may be caused to percolate through a tower filled with the adsorbing material, for example, silica gel, and the refined product drawn off at the bottom of the tower. After the gel has become saturated with impurities from the liquid, the crude is diverted to a second smaller tower, and the gel in the first tower is reactivated.

The preferred method, however, consists in causing a stream of the crude liquid to enter at one end of, and to flow successively through, a series of agitators and separators containing the adsorbing material, for example, silica gel, which is fed in continuously at the end of the apparatus opposite to that at which the liquid enters and by appropriate means is made to move in a direction counter to the liquid flow. In this way, a part of the objectionable constituents of the liquid undergoing refining is removed at each stage as the liquid flows through the apparatus, until finally the refining is completed at the last stage, where the liquid, which has already been deprived of most of its impurities, comes into contact with freshly activated adsorbing material.

The separation of the adsorbed impurities from the adsorbing material may be effected by displacing the adsorbed substance by immersion of the adsorbing material in a liquid which has a lower surface tension than the substance or substances adsorbed at an interface with the adsorbing material, so that the adsorbed substance is replaced by the liquid and then activating the material by driving off or liberating the liquid. For products having higher boiling points, this wash

is not sufficient, and steam activation may be employed as well.

So far as liquids similar to gasoline, kerosene and benzole are concerned, they may be distilled out of gels without difficulty, as by steam activation. The objectionable substances removed by the adsorption, however, often consist of or contain complex organic compounds, usually associated with sulphur, which on heating to a sufficiently high temperature to effect their volatilisation undergo decomposition in the gel, frequently with deposition of carbonaceous and gummy matters which are difficult to remove from the gel, and this difficulty is aggravated in the refining of lubricating oils, waxes *etc.*

In all phenomena connected with adsorption of solutes from liquids, the surface tension at the interface between the solute and the liquid is one of the most important factors determining the degree of adsorption. Since the adsorbing materials employed according to the present invention always contain some water in their pores, the surface tension at the interface of gel and water will be zero, and, therefore, less than the surface tension at the interface of the adsorbing material with other liquids. Accordingly, such porous materials, for example, gels, will adsorb water in preference to another liquid. When a gel which has been saturated with, for example, gasoline (or other liquid immiscible with water), is brought into contact with water, the latter will be adsorbed and the gasoline displaced. If the contact is maintained sufficiently long the displacement of the gasoline will be complete. Furthermore, this water displacement of adsorbed oils may be accelerated by working at a higher temperature.

The present invention comprises a process for the fractional displacement of adsorbed substances from an adsorbent. It has been discovered that when a gel which has adsorbed a mixture of hydrocarbons, such as is obtained by bringing the gel into contact with kerosene, is treated with water, the lighter hydrocarbons are expelled more rapidly than the heavier fractions, particularly if the water is cold. The products associated with the gel are, therefore, recoverable in fractions, and such method of recovery is particularly convenient inasmuch as the most objectionable constituents in unrefined gasoline, which any process of refinement seeks to remove, appear to consist largely of high-boiling hydrocarbons containing sulphur. Hence, the lighter and more valuable fractions of the adsorbed liquid may be displaced by agitation for a limited time with cold water, and the liberated substances removed. The heavier fractions, including most of the objectionable sulphur compounds and other impurities, may then be liberated by agitation, repeatedly if necessary, of the adsorbing material with hot water.

The oil recovered by the cold water displacement is usually of about the same quality as the original unrefined distillate and may be re-run. The very much smaller fraction recovered by hot water agitation consists of relatively high-boiling point constituents of high content in sulphur and unsaturated hydrocarbons, and is suitable for fuel oil.

The product containing over 25 *per cent.* unsaturated hydrocarbons obtained from the pores of the adsorbing material saturated in the refining of a petroleum product, is new. It is free from sulphuric acid and may run as high as 75 *per cent.* or more unsaturated hydrocarbons, and has a specific gravity not lighter than 40° Bé. This product may perhaps be best defined as a product obtained from the pores of a porous material having pores of a size to adsorb not less than 10 *per cent.* of its own weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially 22 m.m. of mercury, which material has been used in refining a petroleum product. This new product is particularly suitable by reason of its high percentage of unsaturated hydrocarbons, for use as a flotation oil in the flotation process of recovering metals.

The gel, or other porous material employed, having been freed by water displacement of the hydrocarbons and other constituents adsorbed from the liquid undergoing refinement, is removed from the wash water and filtered. The resulting gel cake, which now contains practically nothing but water, is run into an activator and its water content reduced to the desired extent usually 6 to 8 *per cent.*, thereby rendering the gel ready for re-use.

The objects and features of novelty of the invention will be apparent from the description taken in connection with the drawings, in which:—

Figure 1 is a diagrammatic view illustrating in elevation one form of apparatus for refining such liquids as petroleum products;

Figure 2 is a sectional elevation of one form of agitator that may be employed in the apparatus;

Figure 3 is a sectional elevation of one form of separator that may be used in the apparatus;

Figure 4 is a sectional plan view taken

substantially on the line 4—4 of Figure 1, showing a feed device; and

Figure 5 is a longitudinal sectional elevation through one form of activator that may be employed.

Referring to the drawings, the liquid to be refined, such as a petroleum, is supplied to a pump 10 by a pipe 11 (Figure 1), and this pump through the pipe 12 feeds the petroleum into an agitator 13. This agitator may be of any suitable construction. As shown, in Figure 2, it may consist of a closed vessel 14 having a vertical shaft 15, provided with blades 16, said shaft projecting above the top of the vessel and having a pulley 17 whereby the shaft is rotated. Suitable adsorbing material, such as silica gel previously mentioned, is supplied through the pipe 18 to the agitator so that the petroleum and gel are thoroughly mixed. The mixture is continuously discharged through the pipe 19 to a separator 20. As shown in Figure 3, this separator, the function of which is to separate the adsorbing material from the liquid, consists of a closed-top vessel having a slightly conical bottom provided with an outlet. A shaft is disposed vertically in the vessel and adjacent the bottom thereof has the deflectors 21 for forcing the adsorbing material, which settles at the bottom, toward the outlet. Around the top of the vessel may be a launder 22. The adsorbing material settles to the bottom of the tank and is discharged through the outlet, while the petroleum product flows into the launder and is carried by a pipe 23 to an agitator 13^2 and a pump 24 acts continuously to supply adsorbing material to said agitator 13^2. The mixture is discharged from this second agitator through a pipe 25 to a second separator 20^2. In the same manner as previously described, the adsorbing material settles to the bottom of this separator and the petroleum is discharged through a pipe 26 into a third agitator 13^3. This agitator is supplied with freshly activated adsorbing material from a hopper 27. The mixture from the agitator is conveyed by the pipe 28 to a third separator 20^3. The refined petroleum is discharged from this separator through a pipe 29. The adsorbing material which settles to the bottom of the third separator is discharged through the outlet in the bottom and conveyed by the pipe 30 to the pump 24, previously mentioned, this pump acting to cause the flow of the adsorbing material. The adsorbing material discharged at the bottom of the second or middle separator is conveyed by a pipe 31 to a pump 45 which discharges into the pipe 18 previously mentioned. This pump 45 effects the flow in the pipe 31.

Although an apparatus having three units, each unit consisting of an agitator and a separator has been described the invention is not limited to any particular number of units.

It will be noted that the fresh, or activated gel is fed into the system to act on the product being refined just before it is finally discharged and then its path through the apparatus is from the discharge end toward the inlet end. Thus, the product fed into the first agitator 13 is mixed with adsorbing material that has already passed through a plurality of separators. This counter-flow of the adsorbing material and the petroleum to be refined gives a very efficient action.

The adsorbing material settling in the bottom of the first separator 20 is discharged into a pipe 33. This adsorbing material has adsorbed impurities from the petroleum and, of course, has petroleum associated therewith. In order to make the process continuous, it is now necessary to free the adsorbing material from its adsorbed substances or "activate" it.

The saturated gel flows through the pipe 33 to a pump 34 which discharges into a water wash agitator 35 of the same construction as the other agitators. Cold water is supplied to this agitator through a pipe 35^1 so that the gel is thoroughly mixed with the water for the purpose of driving out the substances adsorbed in the refining described above. This agitator discharges through a pipe 36 into a separator 37 of the same construction as the other separators, in which the gel settles to the bottom and gasoline or other petroleum products liberated from the gel are carried by the pipe 38 to the agitator 13 so that these products are again run through the refining process. The gel which settles to the bottom of the separator 37 is carried by pipe 39 to the pump 32 which discharges into another agitator 41 supplied with hot water by the pipe 42. This agitator discharges the mixture into another separator 44. The fraction recovered by this hot water agitator, consisting of relatively high-boiling constituents, is discharged through the pipe 46 and may be used for fuel oil, or as a flotation oil. The gel which settles to the bottom of the tank 44 is carried by pipe 47 to pump 48 and discharged through pipe 49 to a filter press 50 of any suitable construction. In this press the surface water is filtered out and the gel cake discharged through the pipe 51 to an activator 52. This activator is illustrated in Figure 5. Briefly stated, it comprises a cylindrical shell 100 with tubes 101 con-

necting the opposite heads 102. The shell is provided with circumferential rings 103 supported by rolls 104 (Figure 1) whereby the cylinder as a whole may be rotated. Hot gases are supplied through the pipe 122 which has communication with the chamber 106. This chamber in turn is in communication with the interior of the tubes 101 so that the hot gases pass through the tubes to the chamber 107 at the opposite end of the cylinder. This chamber is in communication with a suction fan 109 (Figure 1) having the outlet pipe 108. The adsorbing material to be activated is supplied through the conduit 51. If necessary, water, or steam or other gas, may be supplied to the interior of the activator through the inlet 110 which has communication with the centrally disposed tube 111 secured to the head 107. Usually, however, there is sufficient water in the adsorbing material supplied to the activator 52 so that the steam necessary for distilling all the adsorbed substances is supplied from this source. It is the aim of the arrangement to prevent ingress of air to the activator and have the adsorbed substances distilled out of the pores of the adsorbing material, for the reason that if heat as furnished by the hot gases alone is employed for activating the adsorbing material, there is danger of the deposition of carbonaceous and gummy materials within the pores of the adsorbing material. This does not occur where air is excluded from the activator. The dried adsorbing material is discharged through the duct 112 into the intake of the fan 54. The pipe 53 from the fan, discharges the gel or adsorbing material into a cyclone separator 55 wherein the gel settles to the bottom and is discharged into a hopper 56 from which it is fed by a screw conveyor 60 to the hopper 27 which discharges into agitator 13[3] thereby returning the gel into the refining cycle. If desired the gel may be cooled and for this purpose the hopper 27 has its upper portion constructed with cooling surfaces. The vapor and air separated out by the cyclone separator 55 may be discharged into the atmosphere, or, if it is desired to recover any of the vapors or gases, they pass through a pipe 57 to a condenser 58. The condensate and gel not separated by the cyclone separator 55 is drained through a pipe 59 to a pump 60 which discharges through a pipe 61 into the water wash agitator 41.

To prevent any passage of vapors at the lower end of the cyclone separator 55, a novel form of feeding device is employed. As shown in Figure 4, this comprises a plate 85 carried by an oscillating shaft 86 disposed in a box 87, having a hopper bottom 56. The plate 85 is disposed horizontally and is counterbalanced by the weight 88. As shown in Figure 1, the plate is disposed a slight distance below the lower end of the outlet of the cyclone separator 55. The plate is oscillated back and forth in a horizontal plane in any suitable manner, but the extent of oscillation is not sufficient to carry the edges of the plate to either side sufficiently to open up the lower end of the cyclone separator at any time. The oscillation of the plate causes the material to be pushed off the edges of the plate thereby feeding the material forward. For the purpose of oscillating the shaft 86 any suitable mechanism may be employed. As shown, an arm 89 is secured to the upper end of the shaft and outside the box 87. This arm is connected by a link 90 to a crank pin 91 on the crank disc 92, the latter being carried by the armature shaft 93 of the motor 94. In operation, the continual oscillation of the plate 85 effects a uniform feed of the adsorbing material into the hopper 56 but at no time permits passage of vapors.

If desired the discharge from the cyclone separator 55, in addition to being connected to the condenser 58 may have a return pipe 112 for conveying steam to a point adjacent the inlet of the fan 54, as shown at 113. In this manner the steam is used over and over again and a greater volume of gases is supplied to the fan so that the velocity in the pipe 53 is sufficient to raise the adsorbing material therewith. It is to be understood that the pipes 53 and 113 are thoroughly lagged.

In refining some liquids it may happen, after the adsorbing material has made many cycles through the apparatus, that its adsorbing efficiency will be decreased because of the deposition of carbonaceous or gummy materials within its pores. Where this is liable to occur an auxiliary activator may be employed to drive off these substances from the adsorbing material.

As shown this auxiliary activator, in the form of the drum 120, is disposed in the furnace 121 which supplies hot gases through the pipe 122 to the main activator 52. Adsorbing material taken from the hopper 56 or other point may be carried through pipe 123 to the inlet end of the activator 120. This pipe may be supplied with a valve or damper 124 to control the flow of adsorbing material therein. At its discharge end the auxiliary activator 120 has a blower 125 discharging through pipe 126 into a cyclone separator 127. The adsorbing material discharged through this pipe 126

is separated from the air and gases in the cyclone separator 127 and discharged into the cycle at any suitable point, as at the worm conveyor 60. The gases from the top of the cyclone 127 are returned by pipe 128 to the activator 120 at a point adjacent the inlet of the blower 125. In this manner these gases are used over and over to raise the activated adsorbing material. A small quantity of the gases may be exhausted through pipe 128', and the loss made up by air supplied through pipe 123 at the inlet end of the activator. In this manner oxygen is obtained to burn the carbonaceous deposits in the pores of the material. It will be understood that the quantity of adsorbing material supplied to this auxiliary activator may be regulated by valve 124. If desired, all of the adsorbing material from hopper 56 may be passed at intervals through the auxiliary activator 120.

It will be seen, therefore, that a method is provided in which the porous adsorbing material is used over and over in a closed cycle. Not only are the gums already present in the petroleum products removed, but also the compounds capable of forming gums, thereby obtaining a product which will permanently conform to the requirements as to doctor and gum tests, odor and color. Furthermore, the gums are removed without destroying the unsaturated hydrocarbons and the process is, therefore, particularly adapted for the refining of shale oils which may be as high as 90% unsaturated.

It is noted that with the present method the use of sulphuric acid or other chemicals is eliminated, also the losses resulting from the solvent and destructive action of sulphuric acid, particularly upon unsaturated compounds in the product being refined. The process also eliminates any troublesome by-product, such as sludge acid. The refining may be carried to any degree desired. The product may be refined to such an extent that it will have a permanently sweet odor, a permanently negative doctor test, a water white color, even after indefinite exposure to direct sun light in the presence of air and moisture, and a sulphur content as low as 0.1%.

When the present process is employed to refine heavy or viscous oils or waxes, they will be maintained in fluid condition by the application of heat in any suitable manner.

The term "petroleum" or "petroleum products" in the specification and claims are intended to include shale oils.

As previously stated, liquids similar to gasoline, kerosene and benzol may be distilled out of gels without difficulty, as by steam activation. This means that the wash stop is omitted, the gel passing directly from the separator 20 to the filter 50 and then to the activator 52. If necessary, water, steam, or a suitable non-oxydising gas may be admitted at 110.

It is to be understood that the method constituting the present invention is not limited to the apparatus described, as the process may be carried out with other apparatus.

We are aware that it has been proposed to employ special kinds of carbon (see British Specifications Nos. 24,667 of 1910, 132,572 and 163,505), gelatinous precipitates, dried precipitated silica, kieselguhr, Fuller's earth and such like porous materials for the purpose of refining and purifying hydrocarbon oils and other liquids, and it will be understood that we make no broad claim to the use of such materials and that our invention is restricted to the employment of porous adsorbers having pores of the size hereinbefore defined.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of separating dissolved substances or impurities from oils, waxes and the like, particularly petroleum products, by contact treatment of the oil or the like with a porous material, characterised by effecting said treatment with a porous adsorbing material having pores of such size that the material is capable of adsorbing water to the degree to contain not less than substantially ten *per cent.* of its own weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially $22^{m}/_{m}$ of mercury and will adsorb water in preference to other liquids.

2. A process of separating dissolved substances or impurities from oils, waxes and the like, particularly petroleum products, by contact treatment of the oil or the like with a porous material, characterised by effecting said treatment with a mineral oxide gel having pores of such size that the gel is capable of adsorbing water to the degree to contain not less than substantially ten *per cent.* of its own weight of water at 30° C. when in equilibrium with water vapour at a partial pressure of substantially $22^{m}/_{m}$ of mercury.

3. The process of separating dissolved substances or impurities from oils, waxes or the like, particularly petroleum products, characterised by adsorbing the dissolved substances or impurities by contact of the oil or the like with silica gel, or a metallic oxide gel having pores of the size

herein set forth (for example, a gel made according to the process in British Letters Patent No. 212,065).

4. In the separation of dissolved substances or impurities from oils, waxes and the like according to any of the preceding claims, the process of liberating the adsorbed substances from the adsorbing material by distilling them therefrom, for example, by treating said material with steam or with a hot non-oxiding gas, preferably in the absence of air.

5. In the separation of dissolved substances or impurities from oils, waxes and the like according to any of the preceding Claims Nos. 1—3, the process of liberating the adsorbed substances from the adsorbing material by displacing them by a liquid (for example, water) having a lower surface tension towards the adsorbing material than the substance adsorbed, with or without the further step of removing the liquid from the pores of the material for the purpose described.

6. A process according to the preceding Claim, No. 5, characterised by fractionally liberating the adsorbed substances from the adsorbing material, for example, by treatment of the material for a limited time with a liquid of lower surface tension towards the material than the adsorbed substance, separating the so liberated substance, and then repeating the treatment of the material for a more protracted period, or by treating the adsorbing material with a liquid of the said type and thereafter repeating the treatment with the same liquid at a higher temperature.

7. A process according to the preceding Claim No. 6, wherein the adsorbing material (for example, silica gel) contains impurities adsorbed from crude kerosene or like petroleum fraction, characterised by first treating the material with water (for example, at normal temperature) until substantially all the lighter hydrocarbons have been expelled, removing them, and then re-treating the material with water at a higher temperature to effect the expulsion of the heavier hydrocarbons.

8. In the separation of dissolved substances or impurities from oils, waxes and the like according to any of the preceding Claims, Nos. 1—7, the continuous process comprising the removal of the charged adsorbing material from the purifying cycle, freeing the material from the adsorbed substances, reactivating it and returning it to the said cycle.

9. Apparatus for carrying out the process set forth in any one of the preceding claims, comprising means (for example, an agitator 13) to bring the oil or the like to be treated into intimate contact with the adsorbing material whereby substances in solution in the oil are adsorbed, means (for example, a filter or separator 20) to separate the adsorbing material from the oil, and the activator 53 to drive off substances adsorbed in the pores of the adsorbing material.

10. Apparatus according to Claim 9, for separating dissolved substances or impurities from oils and waxes, characterised in that the said activator is provided with discharge means arranged to feed the activated material back to the agitating means for use again therein.

11. Apparatus according to Claim 10 for separating dissolved substances or impurities from oils and waxes, characterised by the provision of a separator (for example, a cyclone separator) in communication with the activator and into which said activator discharges to separate the adsorbing material from vapours mixed therewith before said adsorbing material is used again, with or without means such as a condenser 58 for recovering the vapours from the separator.

12. Apparatus according to Claim 11, wherein in addition to a conduit connecting the activator to the separator, there is provided a return conduit connecting the vapour discharge of the separator to the main activator, for the purpose described.

13. Apparatus according to any one of Claims 9—12, inclusive, wherein an auxiliary activator is provided in addition to the main activator and through which the adsorbing material is passed, for the purpose described.

14. Apparatus according to Claim 11 and for carrying out the process claimed in Claim 5, wherein the adsorbing material, after separation from the oil or the like, is fed to an agitator where it is intimately mixed with a displacing liquid for the purpose described, with or without means for driving off the liquid from the adsorbing material and for returning the adsorbing material for use again, substantially as described.

15. Apparatus for carrying out the process set forth in Claims 5, 6, 7 and 8, comprising in combination an agitator for bringing the oil or the like to be treated into intimate contact with the adsorbing material whereby substances in solution in the oil are adsorbed, a separator arranged to receive the mixture from said agitator to separate the adsorbing material from the oil, a second agitator arranged to receive the adsorbing material which is discharged from said separator and wherein said material is brought into intimate contact with a displacing liquid

for the purpose described, a second separator for separating the adsorbing material from said liquid, an activator arranged to receive the separated adsorbing material from the last-mentioned separator for driving off the liquid adsorbed by said material, and means to return the activated adsorbing material to the first-mentioned agitator.

16. In apparatus according to Claim 11, having an activator and means to supply porous material saturated with adsorbed substances thereto, the provision of means to admit steam to said activator, means to separate the porous material from the vapours discharged from said activator and means to return the vapours to the activator.

17. The improved process for the treatment of oils, waxes, and the like, substantially as described.

18. Refined oils, waxes and the like, and bye-products of their refining, whenever derived by a process as claimed in any one of the preceding process claims.

19. A new petroleum product refined by the process set forth in any one of the above process claims and containing substantially not less than 10 *per cent.* unsaturated hydrocarbons, and having a sulphur content of substantially not more than 0.02 *per cent.*

20. A new flotation oil petroleum product having a specific gravity not lighter than 40° Be. and containing not less than 25 *per cent.* of unsaturated hydrocarbons, said product being obtained from the pores of a porous material which has adsorbed the product from an unrefined petroleum product in a process as set forth in any one of the above process claims.

21. Apparatus for refining oils and waxes and particularly petroleum products, constructed and arranged to operate substantially as herein described with reference to the accompanying drawings.

Dated this 1st day of March, 1923.

BOULT, WADE & TENNANT,
111/112, Hatton Garden, London, E.C. 1,
Chartered Patent Agents.

Reference has been directed in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 and 1919, to Specifications No. 186,955, No. 175,987, No. 163,505 and 24,667 of 1910.

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[Wt. 123A.—25/3/1932.]

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FIG. 1.

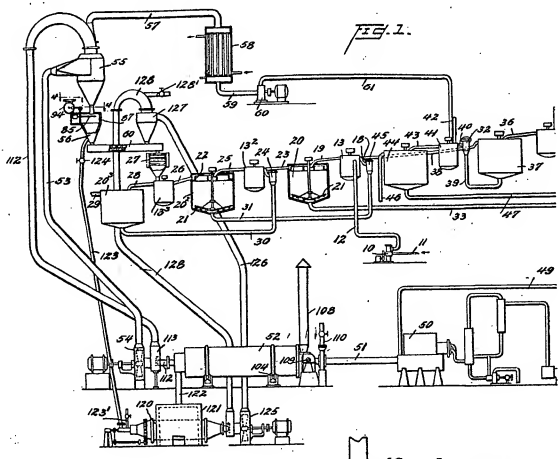
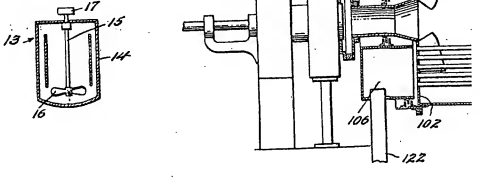


FIG. 2.



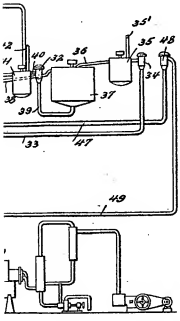
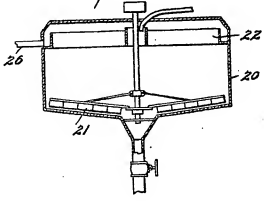


FIG. 3.



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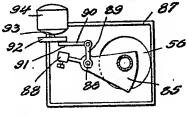

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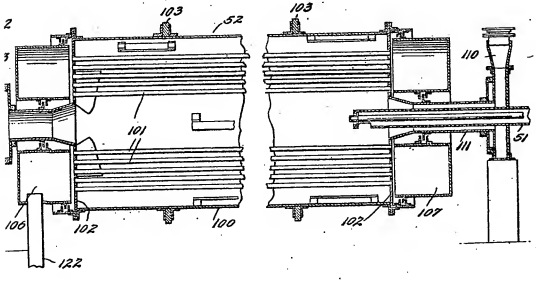

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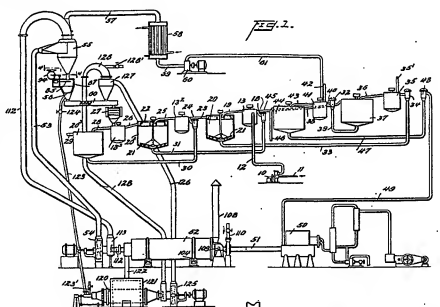

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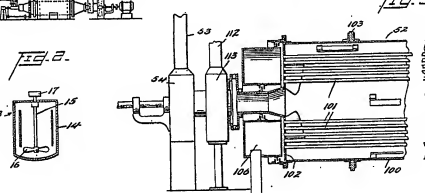

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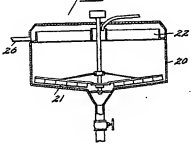

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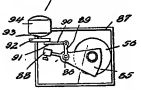

FIG. 5.

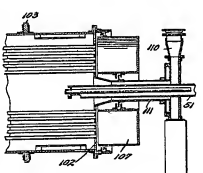

FIG. 6.

[This Drawing is a reproduction of the Original on a reduced scale.]

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